Classical nucleation theory in ordering alloys precipitating with L1$_2$ structure.

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By means of low-temperature expansions (LTEs), the nucleation free energy and the precipitate interface free energy are expressed as functions of the solubility limit for alloys which lead to the precipitation of a stoichiometric L1$_2$ compound such as Al-Sc or Al-Zr alloys. Classical nucleation theory is then used to obtain a simple expression of the nucleation rate whose validity is demonstrated by a comparison with atomic simulations. LTEs also explain why simple mean-field approximation like the Bragg-Williams approximation fails to predict correct nucleation rates in such an ordering alloy.

Since its initial formulation in 1927 by Volmer, Weber and Farkas and its modification in 1935 by Becker and Döring the classical nucleation theory (CNT)[1,2,3] has been a suitable tool to model the nucleation stage in phase transformations. The success of this theory relies on its simplicity and on the few parameters required to predict the nucleation rate. Recently, the use of computer simulations have allowed to assess the applicability of the theory for solid-solid phase transformations[4,5,6,7]. Thanks to a precise control of simulation conditions, it is possible to get accurate estimations of CNT parameters and thus to make a direct comparison between theory predictions and quantities observed during simulations. One thus gains a deeper understanding of the validity of the different assumptions used by the CNT.

Previous studies have shown that the capillary approximation, which CNT relies on, gives a precise description of cluster thermodynamics. Within this approximation, the free energy of a nucleus is written as the sum of a volume contribution, the nucleation free energy, and a surface contribution corresponding to the energy cost to create an interface between the nucleus and the solvent. For CNT to agree with atomic simulations, care has to be taken in the way these two energetic contributions are obtained. In particular, we have shown that one has to take into account short range order when calculating the nucleation free energy in an ordering alloy[4]. Usual thermodynamic approximations, like the ideal solid solution or the Bragg-Williams approximation, cannot describe short range order and thus can predict values of the cluster size distribution and of the nucleation rate wrong by several orders of magnitude. This is to contrast with more sophisticated mean-field approximations like the cluster variation method (CVM) which provides good predictions of the nucleation rate[4]. However, an easy use of CNT and a clear determination of the missing ingredients in simple mean-field approximations requires an analytical approach which CVM cannot provide. Such an approach has to lead to accurate expressions of the CNT input parameters so as to make the theory predictive without any fitting of its parameters.

In this Letter, we use low-temperature expansions (LTE)[8,9] to derive an analytical formulation of the nucleation free energy and the interface free energy in a binary system like Al-Sc or Al-Zr, *i.e.* a supersaturated Al-X solid solution leading to the nucleation of a stoichiometric Al$_3$X compound with the L1$_2$ structure. This structure corresponds to an ordering of the fcc lattice with solute X atoms lying on one of the four cubic sublattices[8]. LTE are well suited to describe short range order in dilute solid solution and nearly stoichiometric ordered compounds[10,11,12,13,14] like Al$_3$X compound. The use of this method in CNT framework allows to obtain a fully analytical modelling whose only material parameters are the solubility limit and the solute diffusion coefficient.

To do so, we start from the same atomic diffusion model previously developed for Al-Sc-Zr system[4,15]. This model relies on a rigid lattice with interactions between first- and second nearest neighbors and uses a thermally activated atom-vacancy exchange mechanism to describe diffusion. Despite its simplicity, it has been shown to lead to predictions in good agreement with experimental data[15,16,17]. Within this atomic model, atoms are constrained to lie on a fcc lattice and the configurations of a binary Al-X alloy is fully described by the solute atom occupation number p_n with $p_n = 1$ if the site n is occupied by a solute atom and $p_n = 0$ otherwise. The energy per atom of a given configuration of the Al-X alloys is then given by

$$E = U_{\mathrm{Al}} + \frac{1}{N_s}\left(U_{\mathrm{X}} - U_{\mathrm{Al}}\right)\sum_n p_n$$
$$+ \frac{1}{N_s}\omega_{\mathrm{AlX}}^{(1)}\sideset{}{'}\sum_{n,m}\left(1 - p_n\right)p_m$$
$$+ \frac{1}{N_s}\omega_{\mathrm{AlX}}^{(2)}\sideset{}{''}\sum_{n,m}\left(1 - p_n\right)p_m \quad (1)$$

where the first and second sums, respectively, run on all first and second nearest-neighbor pairs of sites, N_s is the number of lattice sites, U_{Al} (respectively U_{X}) is the energy per atom when only Al (respectively X) atoms lie on the fcc lattice and $\omega_{\mathrm{AlX}}^{(1)}$ and $\omega_{\mathrm{AlX}}^{(2)}$ are the first and second nearest neighbor order energies. Al-Sc and Al-Zr thermodynamics are characterized by the order tendency between first nearest neighbors ($\omega_{\mathrm{AlX}}^{(1)} < 0$) and the demixing tendency between second nearest neighbors ($\omega_{\mathrm{AlX}}^{(2)} > 0$). Eq. 1 is a rewriting for binary alloys of the atomic model developed in Refs.[4,15] when one neglects vacancy contributions.

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The nucleation free energy entering CNT is defined by

$$\Delta G^{\mathrm{nuc}}(x_{\mathrm{X}}^0) = \frac{3}{4}\left[\mu_{\mathrm{Al}}(x_{\mathrm{X}}^{eq}) - \mu_{\mathrm{Al}}(x_{\mathrm{X}}^0)\right]$$
$$+ \frac{1}{4}\left[\mu_{\mathrm{X}}(x_{\mathrm{X}}^{eq}) - \mu_{\mathrm{X}}(x_{\mathrm{X}}^0)\right], \quad (2)$$

where $\mu_{\mathrm{Al}}(x_{\mathrm{X}})$ and $\mu_{\mathrm{X}}(x_{\mathrm{X}})$ are the Al and X component chemical potentials in a solid solution of concentration x_{X}, and x_{X}^{eq} and x_{X}^0 the concentrations of the equilibrium and supersaturated solid solution.

LTE are more easy to handle in semi-grand-canonical ensemble where all quantities are written as functions of the effective potential $\mu = (\mu_{\mathrm{Al}} - \mu_{\mathrm{X}})/2$. Definition of the nucleation free energy then becomes

$$\Delta G^{\mathrm{nuc}}(\mu) = \mathcal{A}(\mu^{\mathrm{eq}}) - \mathcal{A}(\mu) + \frac{1}{2}(\mu^{\mathrm{eq}} - \mu), \quad (3)$$

where μ^{eq} is the effective potential corresponding to equilibrium between the Al solid solution and the Al$_3$X L1$_2$ compound. We have defined in Eq. 3 the solid solution semi-grand-canonical free energy $\mathcal{A} = (\mu_{\mathrm{Al}} + \mu_{\mathrm{X}})/2 = F(x) + (1-2x)\mu$, $F(x)$ being the usual canonical free energy.

A LTE consists in developing the partition function of the system around a reference state, keeping in the series only the excited states of lowest energies. Use of the linked cluster theorem[8,9] allows then to express the corresponding semi-grand canonical free energy as

$$\mathcal{A}(\mu) = \mathcal{A}^0(\mu) - kT \sum_{i,n} g_{i,n} \exp\left(-\Delta E_{i,n}(\mu)/kT\right), \quad (4)$$

where the energy of the ground state is $\mathcal{A}^0(\mu) = U_{\mathrm{Al}} + \mu$ for the Al solid solution and $\mathcal{A}^0(\mu) = 3/4\,U_{\mathrm{Al}} + 1/4\,U_{\mathrm{X}} + 3\omega_{\mathrm{AlX}}^{(1)} + \mu/2$ for the Al$_3$X L1$_2$ compound. In the sum appearing in Eq. 4, the excited states have been gathered according to their energy state i and the number n of lattice sites involved. LTE parameters corresponding to the excited states with the lowest energies are given in Tab. I. All excitation energies only involve a set of isolated atoms or in second nearest neighbor position since flipping two atoms at nearest neighbor position produces an excited state with a much higher energy.

The solute concentration in a given phase is obtained by considering the derivative of the corresponding semi-grand-canonical free energy. For the solid solution, one gets

$$x_{\mathrm{X}}(\mu) = \frac{1}{2}\left(1 - \frac{\partial \mathcal{A}(\mu)}{\partial \mu}\right)$$
$$= \sum_{i,n} n g_{i,n} \exp\left(-\Delta E_{i,n}(\mu)/kT\right). \quad (5)$$

The solid solution and the L1$_2$ compound are in equilibrium when both phases have the same semi-grand canonical free energy. Considering third order LTE

TABLE I: Coefficients entering in the low temperature expansion (Eq. 4). The first seven excited states are considered for the solid solution and the first three excited states for the Al$_3$X L1$_2$ compound. The effective potential is written as $\mu = (U_{\mathrm{X}} - U_{\mathrm{Al}})/2 + 6\omega_{\mathrm{AlX}}^{(1)} + \delta\mu$.

			Solid solution		L1$_2$ compound	
i	n		$\Delta E_{i,n}(\mu)$	$g_{i,n}$	$\Delta E_{i,n}(\mu)$	$g_{i,n}$
1	1	•	$6\omega_{\mathrm{AlX}}^{(2)} - 2\delta\mu$	1	$6\omega_{\mathrm{AlX}}^{(2)} + 2\delta\mu$	1/4
2	2		$10\omega_{\mathrm{AlX}}^{(2)} - 4\delta\mu$	3	$10\omega_{\mathrm{AlX}}^{(2)} + 4\delta\mu$	3/4
3	2		$12\omega_{\mathrm{AlX}}^{(2)} - 4\delta\mu$	$-19/2$	$12\omega_{\mathrm{AlX}}^{(2)} + 4\delta\mu$	$-7/8$
4	3		$14\omega_{\mathrm{AlX}}^{(2)} - 6\delta\mu$	15		
5	4		$16\omega_{\mathrm{AlX}}^{(2)} - 8\delta\mu$	3		
5	3		$16\omega_{\mathrm{AlX}}^{(2)} - 6\delta\mu$	-96		
6	4		$18\omega_{\mathrm{AlX}}^{(2)} - 8\delta\mu$	83		
6	3		$18\omega_{\mathrm{AlX}}^{(2)} - 6\delta\mu$	-774		
7	5		$20\omega_{\mathrm{AlX}}^{(2)} - 10\delta\mu$	48		
7	4		$20\omega_{\mathrm{AlX}}^{(2)} - 8\delta\mu$	$-1569/2$		

$(i = 3)$, this happens for the effective potential

$$\mu^{\mathrm{eq}} = (U_{\mathrm{X}} - U_{\mathrm{Al}})/2 + 6\omega_{\mathrm{AlX}}^{(1)}$$
$$+ \frac{3}{2}kT\left[\exp\left(-6\omega_{\mathrm{AlX}}^{(2)}/kT\right) + 3\exp\left(-10\omega_{\mathrm{AlX}}^{(2)}/kT\right)\right.$$
$$\left. - \frac{13}{2}\exp\left(-12\omega_{\mathrm{AlX}}^{(2)}/kT\right)\right], \quad (6)$$

corresponding to the solubility

$$x_{\mathrm{X}}^{\mathrm{eq}} = \exp\left(-6\omega_{\mathrm{AlX}}^{(2)}/kT\right) + 6\exp\left(-10\omega_{\mathrm{AlX}}^{(2)}/kT\right)$$
$$- 16\exp\left(-12\omega_{\mathrm{AlX}}^{(2)}/kT\right). \quad (7)$$

As these expressions have to be consistent with the expansion of $\mathcal{A}$, terms with larger exponential arguments than $-12\omega_{\mathrm{AlX}}^{(2)}$ are discarded. For equilibrium phases, one does not need to go further in the expansion than the third order. Indeed, thermodynamic properties are already well converged as the solid solution and the L1$_2$ compound in equilibrium only slightly deviate from their respective ground states. On the other hand, Fig. 1 show that an expansion beyond the third order of the semi-grand canonical free energy $\mathcal{A}(\mu)$ of the supersaturated solid solution and of the corresponding concentration $x_{\mathrm{X}}(\mu)$ improves the convergence of the nucleation free energy. When only the first excited state is included in the expansion, LTE leads to the same value of the nucleation free energy as the ideal solid solution model. As more excited state are included in the expansion, the value deduced from LTE converges to the one calculated with CVM in the tetrahedron-octahedron approximation[4]. This is to contrast to the Bragg-Williams approximation which leads to a worse prediction of the nucleation free energy than the ideal solid solution model.
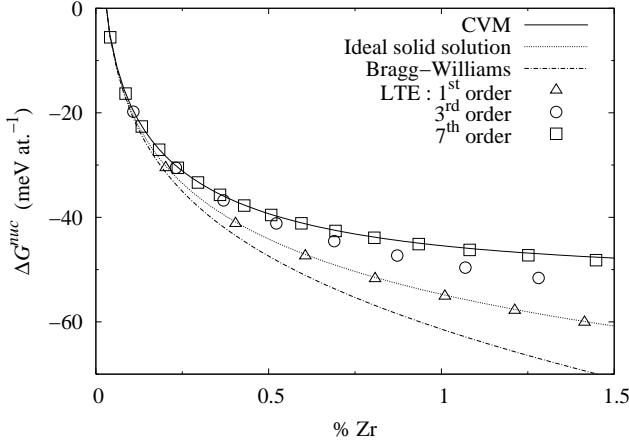
FIG. 1: Variation with the nominal concentration x_{Zr}^0 of the nucleation free energy ΔG^{nuc} at $T = 723$ K obtained with different thermodynamic approximations: CVM, ideal solid solution, Bragg-Williams and low-temperature expansions (LTE) to different orders.

So as to understand why Bragg-Williams approximation does so bad, it is worth going back to the canonical ensemble. When considering only the third order LTE, thermodynamic quantities can be expressed as functions of the solid solution nominal concentration x_X^0. In particular, the nucleation free energy is given by

$$\Delta G_{LTE}^{nuc}(x_X^0) = kT \left[q\left(x_X^0\right) - q\left(x_X^{eq}\right) \right]$$
$$+ 3kT \exp\left(2\omega_{AlX}^{(2)}/kT\right) \left[q\left(x_X^0\right)^2 - q\left(x_X^{eq}\right)^2 \right]$$
$$- \frac{1}{4}kT \left\{ \ln\left[q\left(x_X^0\right)\right] - \ln\left[q\left(x_X^{eq}\right)\right] \right\}, \quad (8)$$

where we have defined the function

$$q(x) = \frac{2x}{1 + \sqrt{1 + 4x \left[6 \exp\left(2\omega_{AlX}^{(2)}/kT\right) - 19 \right]}}. \quad (9)$$

This expression developed to first order in the concentrations x_X^0 and x_X^{eq} leads to

$$\Delta G_{LTE}^{nuc}(x_X^0) \sim \frac{3}{4}kT \ln\left(\frac{1 - x_X^{eq}}{1 - x_X^0}\right) + \frac{1}{4}kT \ln\left(\frac{x_X^{eq}}{x_X^0}\right)$$
$$+ \frac{1}{4}kT \left(1 + 6e^{2\omega_{AlX}^{(2)}/kT}\right)\left(x_X^0 - x_X^{eq}\right). \quad (10)$$

Doing the same development for the nucleation free energy calculated within the Bragg-Williams approximation[4], we obtain

$$\Delta G_{BW}^{nuc}(x_X^0) \sim \frac{3}{4}kT \ln\left(\frac{1 - x_X^{eq}}{1 - x_X^0}\right) + \frac{1}{4}kT \ln\left(\frac{x_X^{eq}}{x_X^0}\right)$$
$$+ \left(6\omega_{AlX}^{(1)} + 3\omega_{AlX}^{(2)}\right)\left(x_X^0 - x_X^{eq}\right). \quad (11)$$

Comparing Eq. 10 with Eq. 11, we see that these two thermodynamic approximations deviate from the ideal solid solution model by a distinct linear term. In the LTE (Eq. 10), the nucleation free energy is only depending on the second nearest neighbor interaction and the coefficient in front of the concentration difference is positive. On the other hand, the Bragg-Williams approximation (Eq. 11) incorporates both first and second nearest neighbor interactions into a global parameter $\omega_{AlX} = 6\omega_{AlX}^{(1)} + 3\omega_{AlX}^{(2)}$. This leads to a linear correction with a coefficient which can be negative due to the oscillating nature of the interactions. In particular, this is the case for both binary Al-Zr and Al-Sc alloys[4]. Bragg-Williams approximation thus leads to a wrong correction of the ideal model because it does not consider properly short range order. In the case of a L1$_2$ ordered compound precipitating from a solid solution lying on a fcc lattice, one cannot use such an approximation to calculate the nucleation free energy. On the other hand, Eq. 8 is a good approximation and can be used to calculate the nucleation free energy even when the second nearest neighbor interaction $\omega_{AlX}^{(2)}$ is not known. Indeed, this parameter can be deduced from the solubility limit x_X^{eq} by inverting Eq. 7, leading to the relation

$$\omega_{AlX}^{(2)} = -\frac{1}{6}kT \ln\left(x_X^{eq}\right) + kT \left(x_X^{eq2/3} - \frac{8}{3}x_X^{eq}\right). \quad (12)$$

This relation combined with Eq. 8 provides a powerful way for calculating the nucleation free energy from the solid solubility.

LTE can be used too to calculate the plane interface free energy σ_{100} corresponding to a [100] direction. Due to the inhomogeneity perpendicular to the interface, the main contribution arises from broken bonds and excited states, whose energies are lower than in bulk phases, only bring a small correction. One thus does not need to go further than the second order in the expansion. At 0 K, the isotropic interface free energy $\bar{\sigma}$ is obtained by multiplying σ_{100} with the geometric factor $(6/\pi)^{1/3}$ corresponding to a perfect [100] facetting of the precipitates. For low temperatures, this is a good approximation to assume that the same linear relation holds between both quantities[4]. The isotropic interface free energy given by LTE is then

$$a^2\bar{\sigma} = (6/\pi)^{1/3} \left[\omega_{AlX}^{(2)} - 2kT \exp\left(-4\omega_{AlX}^{(2)}/kT\right) \right.$$
$$\left. -kT \exp\left(-6\omega_{AlX}^{(2)}/kT\right) \right], \quad (13)$$

where a is the fcc lattice parameter.

LTE thus allow to calculate all CNT input parameters from the knowledge of the solubility limit. The nucleation rate is then obtained from the equation

$$J^{st}(x_X^0) = -16N_s \frac{\Delta G^{nuc}(x_X^0)}{\sqrt{kT a^2 \bar{\sigma}}} \frac{D_X}{a^2} x_X^0$$
$$\exp\left(-\frac{\pi}{3} \frac{(a^2\bar{\sigma})^3}{kT[\Delta G^{nuc}(x_X^0)]^2}\right), \quad (14)$$
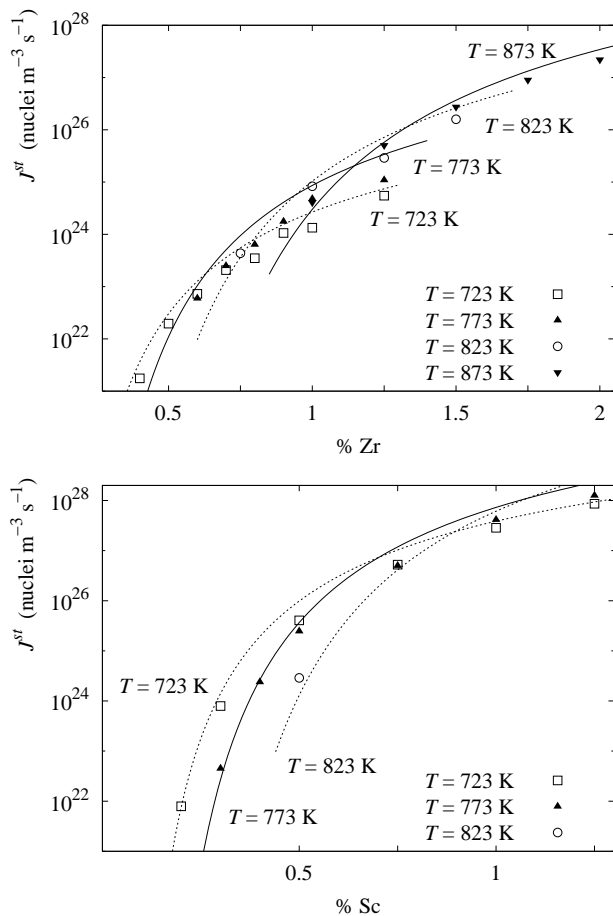
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FIG. 2: Variation with nominal concentration and temperature of the steady-state nucleation rate J^{st} for Al_3Zr (top) and Al_3Sc (bottom) precipitations. Symbols correspond to kinetic Monte Carlo simulations and lines to classical nucleation theory

where D_X is the X impurity diffusion coefficient in Al. We thus obtain a fully analytical expression of the nucleation rate. Using the same experimental data, *i.e.* solubility limits and diffusion coefficients, as the ones used to fit the atomic diffusion model of kinetic Monte Carlo simulations, we can compare CNT predictions with nucleation rate observed in simulations[4]. A good agreement is obtained both for Al-Zr and Al-Sc binary alloys (Fig. 2).

The combination of LTE with CNT thus allows to build a quantitative modeling of nucleation relying on a very limited number of material parameters. Such a model can be directly applied to aluminum alloys where a $L1_2$ compound precipitates from a supersaturated solid solution as this is the case with Zr, Sc or other rare earth elements like Er, Tm, Yb and Lu[18]. Li too precipitates in aluminum with a $L1_2$ structure, but this system requires another statistical approximation than LTE. Indeed, this approach based on LTE, requires that the precipitating phase only slightly deviates from its perfect stoichiometry and that the solute solubility remains low. Provided these conditions are fulfilled, it could be applied to alloys other than aluminum alloys. More generally, LTE demonstrate that the oscillating nature of the interactions in an alloy with an ordering tendency has to be taken into account by the CNT and requires a better statistical description than the Bragg-Williams approximation which treats all interactions on the same footing.

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